CEMENT AND LIME MANUFACTURE

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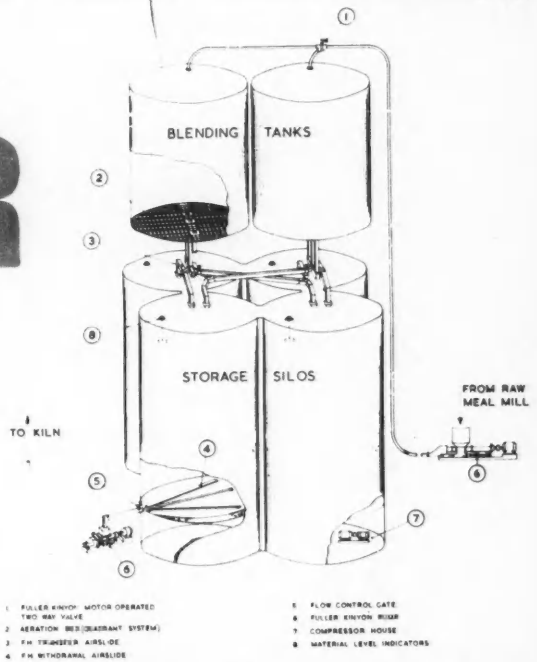

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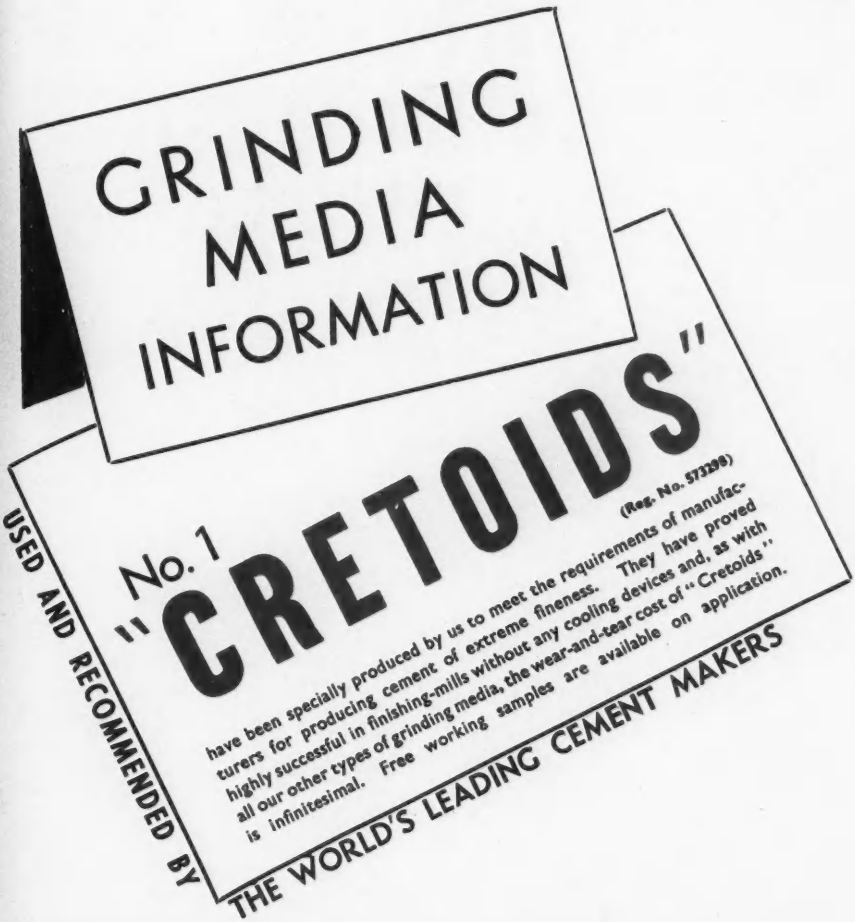
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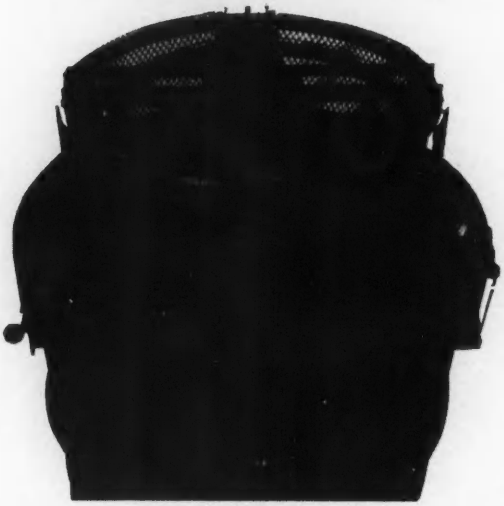

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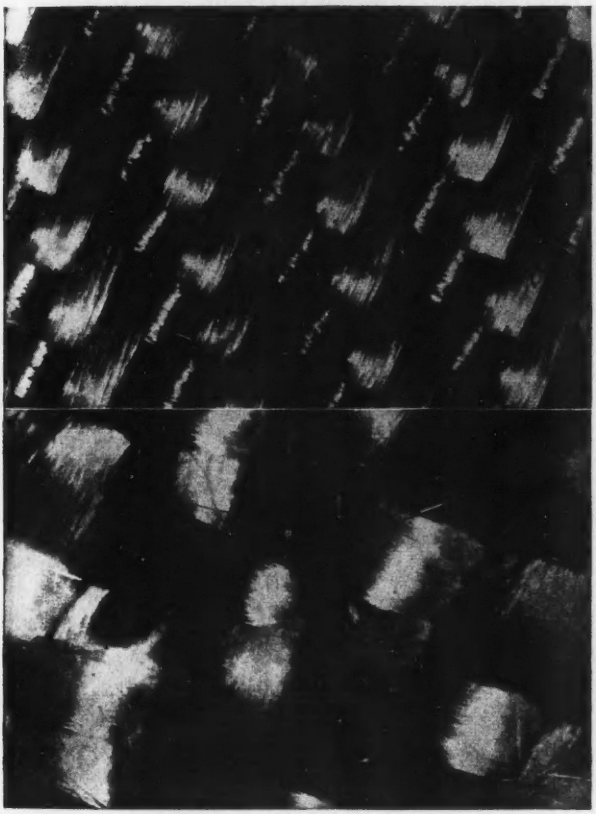

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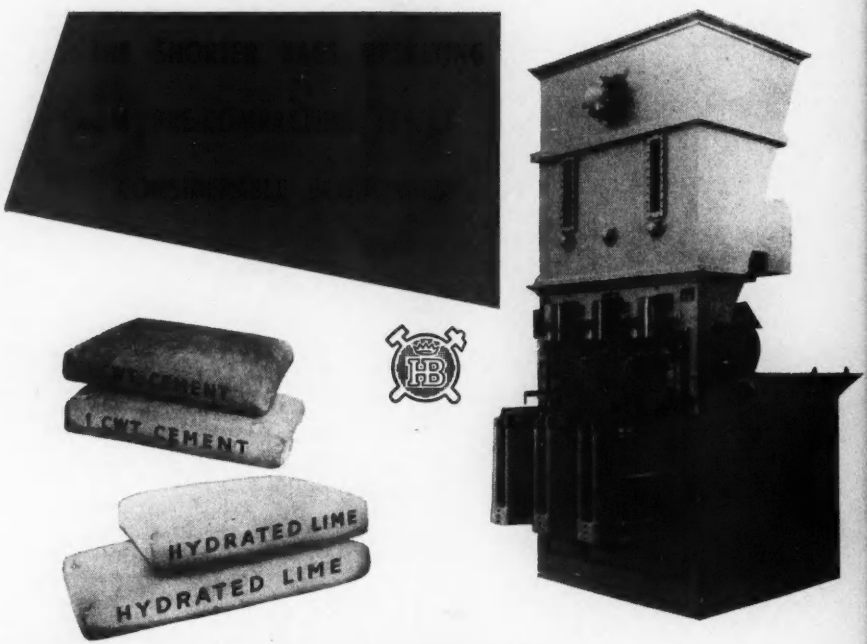

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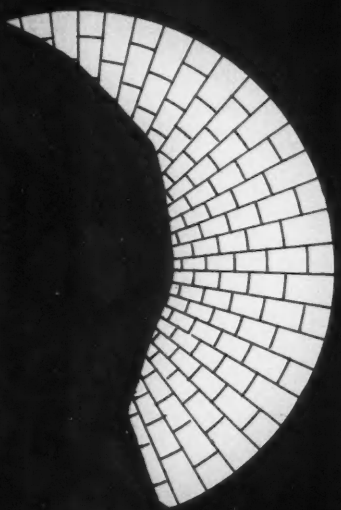

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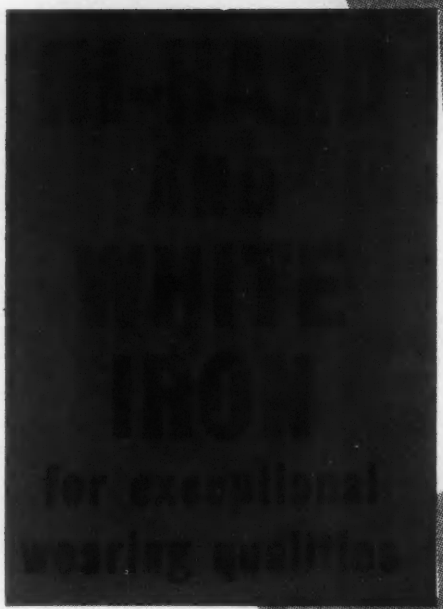

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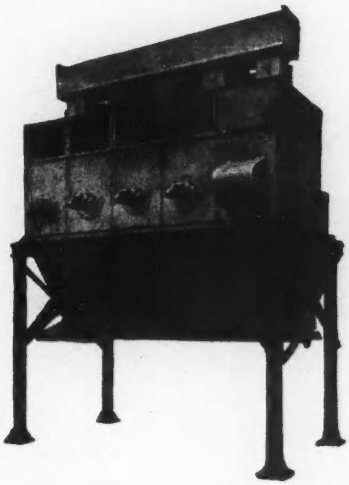

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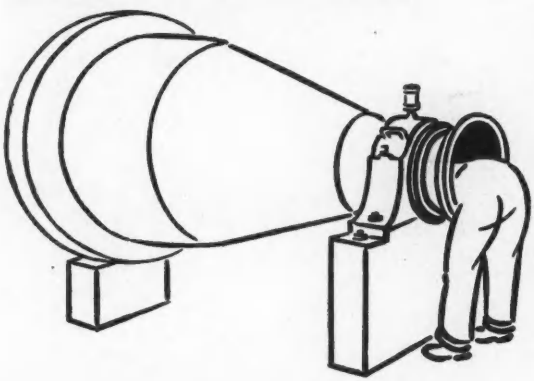

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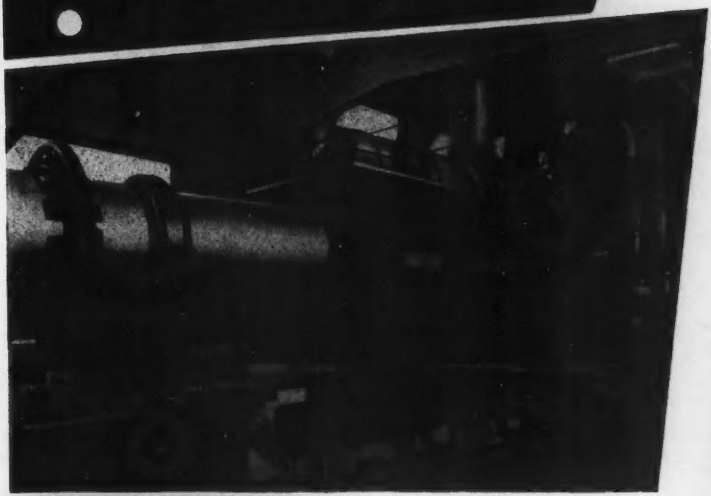

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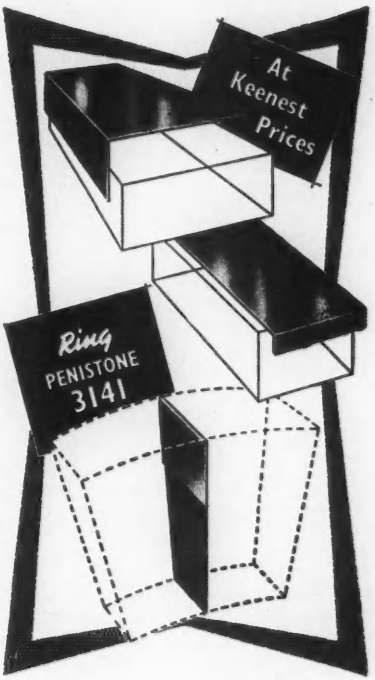

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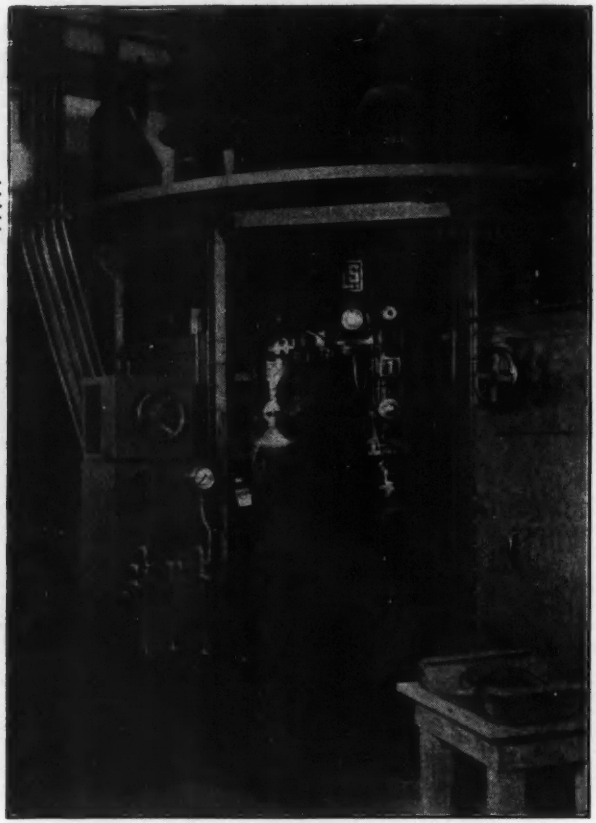

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VOLUME XXXII. NUMBER 5. SEPTEMBER, 1959

The Examination of Samples from a Rotating Kiln.

A METHOD of taking samples from a cement kiln while it is in operation, and some of the results, are described by Mr. T. Palvio (Chief Chemist of the St. Lawrence Cement Company, of Canada) in " Pit and Quarry " for July 1959. The following is an abstract of the article.

The wet-process kilns of the St. Lawrence Cement Company at Clarkson are provided, in the preparation and calcining zones, with eight sample-holes which can be opened while the kiln is in operation by removing the caps. The material flows from the kiln and can be collected in a pail. A representative sample is taken, and the temperature is measured.

The positions of the sample-holes and the chains are shown in *Fig.* 1, which also gives the analytical data concerning moisture, temperature, free lime, alkalis, and sulphur. The moisture content was determined at 110 deg. C., the free lime by the ethylene glycol-methyl-alcohol method, the alkalis with a Beckman DU spectrophotometer, the total sulphur content was determined gravimetrically as $BaSO_4$, and the sulphide sulphur was determined with I_2 standard solution back-titrated with $Na_2S_2O_3$. Except for the moisture and the free lime the results are based on loss-free samples, that is on the basis of the clinker. For the purpose of the calculations the loss on ignition was determined by heating at 1,050 deg. C. for half an hour. As is seen in the figure, no sample was taken from hole No. 1 because experience had shown that the slurry there was too wet for sampling.

Fig. 1 shows that the raw mixture was completely dry at the end of the chains (hole No. 4); this indicates that the last portion of the chains forms the dust. The dust-injection principle developed by Mr. H. W. Mooser (U.S. patent No. 2,477,262, July 26, 1949) is used. The collected dust is injected into the burning zone through the flame, and the result is increased production and greater efficiency of heating.

The total amount of dust generated may be estimated from the quantitative

analysis of K_2O in the raw mixture, returned dust, and samples from hole No. 2, which is the point at which no more dust is formed because of the high moisture content. The results based on dry materials are as follows: Raw mixture, 0·82 per cent. K_2O; return dust, 4·47 per cent.; sample-hole No. 2, 1·68 per cent.

As a large amount of dust is caught by the wet chains, the dust actually circulating is estimated to be about 4 to 8 per cent. of the dry raw material. The amount of dust at hole No. 2 may also be calculated from the results obtained

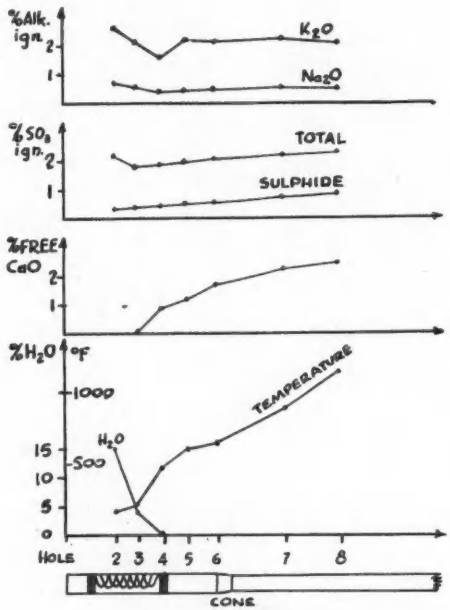


Fig. 1.—Results of Tests.

from the analysis of the total quantity of SO_3 present, which can be determined accurately.

The temperature curve in *Fig.* 1 indicates the efficiency of the transference of heat taking place in the dry chains; the chain-section makes relatively low kiln-exhaust temperatures (450 deg. F.) possible. The efficiency of the exchange of heat increases in the slimmer calcining zone, where the velocity of the gas is high. However, the rate of increase of temperature in the dry-chain area of the kiln is greater.

The raw materials have a small sulphur content, but the coal fuel contains about 3 per cent. of sulphur. The sulphide-sulphur curve suggests continuous and rather uniform oxidisation of sulphides within the range tested. The returned

dust contains about 0·4 per cent. of sulphur, but none is present in the clinker. Apparently the sulphides originating from coal swept into the kiln with the injected dust are deposited throughout the length of the kiln, while some escape to the dust collectors. About one-half of the quantity of sulphides is soluble in water.

A feature of *Fig.* 1 is the similarity of the shapes of the curves for K_2O and Na_2O; yet the K_2O curve, having a sharper angle at its minimum point, suggests that a large portion of kiln dust is caught in the wet chains. In the drier parts of the chain-section the concentration of alkali is reduced, probably because the particles are smaller and higher. Theoretically, a reduction of alkali should result if the finest dust were removed from the precipitator system, or if a larger, denser, or generally "dustier" dry-chain section were installed. Beyond the chain section the content of alkali increases, suggesting that the rate of depositing dust exceeds that of dusting.

In the clinker most of the alkalis appear in the form of potassium or sodium sulphates. Sulphates are harder to volatilise if alkalis are present in excess in sulphates. The sulphate phase may contain K_2O and Na_2O in a molecular ratio up to 3 to 1. The rest of the alkalis are reported to form $KC_{23}S_{12}$ and NaC_8A_3. The dust injected through the flame is expected to undergo better alkali-volatilisation by being exposed to higher flame temperatures, in addition to its movement through the burning zone in the form of clinker.

As is generally known, potassium volatilises more readily than sodium in most cement kilns. This is the case here, where the following ratios of K_2O to Na_2O by weight were observed: Raw material, 3·77; clinker, 2·73; average kiln sample, 4·26; muliticlone, 9·4; electrofilter (total), 10·2; electrofilter (compartment 3), 11·3; loss in stack, 11·4.

The test described was carried out under normal operating conditions. The amount of water in the slurry was 33·8 per cent., the residue on a 200-mesh sieve was 18·1 per cent., the rate of production was 1,110 tons daily, the temperature of the gas before the chains was 1,400 deg. F., the oxygen in the exit-gas was 2·7 per cent., and the dimensions of the kiln were 402 ft. by diameters of 13 ft. 2 in., 11 ft. 6 in., and 13 ft. 2 in.

French Cement Makers Honoured.

Each year the French society Prestige de la France awards a diploma to an organisation or firm whose activities are judged to have been outstanding in gaining repute for French industry throughout the world. The award for 1958 has been made to Etablissements Poliet et Chausson, the largest makers of cement, lime, and plaster in France. Founded in the year 1901, the firm operates six cement works, a lime works, four factories producing plaster, and a factory for special products. It is stated that the kiln at the firm's cement works at Gargenville is the second largest in the world. The production of cement by the firm in 1958 was 2,500,000 tons.

U.S.A. Standards for Lime.

THE U.S.A. standard and tentative specifications and methods of testing lime are printed in full in the triennial publication* of the collected standards of the American Society for Testing Materials. The definition of terms relating to lime is given in Standard C51 (1947).

The standard specifications are Quicklime for Structural Purposes (C5–1926), Normal Finishing Hydrated Lime (C6–1949), Special Finishing Hydrated Lime (C206–1949), Hydrated Lime for Masonry Purposes (C207–1949), Hydraulic Hydrated Lime for Structural Purposes (C141–1955), Quicklime and Hydrated Lime for Cooking of Rags in Paper Manufacture (C45–1925), Quicklime for Sulphite Pulp Manufacture (C46–1927), Quicklime and Hydrated Lime for Silica Brick Manufacture (C49–1957), Quicklime for Calcium Carbide Manufacture (C258–1952), and Hydrated Lime for Grease Manufacture (C259–1952).

The tentative specifications are Quicklime and Hydrated Lime for Water Treatment (C53–1952), Fly Ash for Use as a Pozzolanic Material with Lime (C379–1956), and Inorganic Aggregates for Use in Gypsum Plaster (C35–1957).

A new tentative specification is for Quicklime and Hydrated Lime for Sand-Lime Products (C415–1958). The principal chemical requirements are that the lime shall not contain more than 2½ per cent. of CO_2, and that the composition shall be not less than 90 per cent. of CaO, not more than 2·5 per cent. of MgO, not more than 1·5 per cent. of combined Fe_2O_3 and Al_2O_3, and not more than 3 per cent. of SiO_2 and insoluble matter. The fineness must be such that not less than 99 per cent. passes a No. 30 sieve and not less than 95 per cent. passes a No. 200 sieve.

The methods of chemical analysis (C25–1958) and physical testing (C110–1958) of limestone, quicklime, and hydrated lime were revised in 1958. There is also a tentative method of testing these materials for neutralisation of waste acid (C400–1957).

The methods of sampling, inspection, packing, and marking of lime and limestone products are described in Standard C50–1957.

* A.S.T.M. Standards 1958 Part 4.—Cement, Concrete, Mortars, Road Materials, Waterproofing and Soils. Price 12 dollars. Obtainable from the Society at 1916 Race Street, Philadelphia.

A Long Cement Kiln.

A rotary kiln 550 ft. in length and 15 ft. in diameter, and with a capacity of 8000 barrels (about 1330 tons) a day, is to be installed by Allis-Chalmers International (U.S.A.) at a cement works to be built at Montreal, Canada, for Messrs. Miron & Freres, Ltd. The kiln will have an air-quenching cooler, 12 ft. long by 7 ft. 6 in. diameter, of the counterbalance type.

Investigation of Raw Materials of High Silicate Modulus.

The possibility of making satisfactory cement clinker by burning materials with an unusually high silicate modulus has been investigated by Klaus Dyckerhoff, and the following is a summary of his report in " Zement-Kalk-Gips " for May, 1958.

A silicate modulus (SiO_2/R_2O_3) of about 4 is normally regarded as the upper limit for a cement mixture which will produce satisfactory clinker. Since certain siliceous limestones with silicate moduli as high as 12 can be burned satisfactorily, the causes of this were sought in natural materials with a range of silicate moduli. Siliceous limestones from Bologna in Italy (silicate modulus 5·5) and Novorossiysk in the Soviet Union (silicate modulus 11·7) were selected; these are natural materials from which satisfactory cement clinker is manufactured. From Le Tiel in France were selected a pure type of limestone (No. 1 with a silicate modulus of 24·3) and a siliceous limestone with the composition of a raw mixture of high silicate modulus (No. 11, silicate modulus 19·5). The fifth material was a natural material from Buenos Aires consisting of pure limestone and pyrophyllite, containing quartz. None of these materials contained appreciable amounts of any constituent not normally present in an ordinary cement mixture. Contents of alkali were small (K_2O, 0·02 to 0·38 per cent.; Na_2O, 0·8 to 0·13 per cent.).

The residues insoluble in cold twice-normal hydrochloric acid were studied by means of X-rays to determine whether a form of silica other than quartz was present, to which might be attributed special behaviour on burning. Only quartz was recognisable in the material from Novorossiysk and material No. 1 from Le Tiel. The specimen from Bologna contained quartz with small amounts of illite. The sample from Buenos Aires contained pyrophyllite and muscovite in addition to quartz.

Specimens of the materials from Bologna and Novorossiysk and of the No. 1 material from Le Tiel, which were in the form of stone, were polished for microscopic examination. The harder silicic acid component was polished into relief from the softer calcite. The stone from Bologna contained veins and flecks of calcite; crystals of calcite were recognised in polarised light. The quartz was in the form of particles not greater than 15μ in diameter; most of the particles were very much finer. The calcite in the stone from Novorossiysk occurred only in flecks, without veins, and the quartz was very fine and uniform in some parts but up to 15μ in others. No. 1 limestone from Le Tiel was irregular in composition, with quartz particles up to 70μ. In all three cases most of the quartz was substantially finer than 10μ. The distribution of the sizes of the quartz grains was determined by treating a weighed sample of material with twice-normal hydrochloric acid, washing the residue free of chlorine, and transferring it directly to an Andreason sedimentation apparatus. In a parallel extraction, the residue was dried at 105 deg. C. to ascertain its actual weight and specific gravity.

Only the material from Buenos Aires contained an appreciable amount (about

51 per cent.) of quartz particles larger than 20μ. (Bologna: 98 per cent. smaller than 20μ, 92 per cent. smaller than 10μ; Novorossiysk: 94 per cent. smaller than 20μ, 87 per cent. smaller than 10μ.)

As the microscope showed that the silicic acid component was very fine and was evenly distributed in the materials from Bologna and Novorossiysk, lumps of these stones were burned at 1450 deg. C. for 45 minutes to determine how the veins and flecks of calcite participated in the reaction. The polished specimen of clinker, after etching with dimethylamine citrate, showed C_3S, C_2S, and free lime. With the silicate modulus of 5·5 of the material from Bologna, the ground-mass was clearly visible. Veins of calcite showed as free lime. A vein 0·1 to 0·13 mm. in width was enclosed in C_3S with C_2S at a distance of not less than 0·4 mm., and there was always a sharp boundary between the C_3S and C_2S parallel to the vein. In the material from Novorossiysk with the silicate modulus of 11·7 no ground-mass was visible. The former flecks of calcite remained as zones of free lime.

Samples of these two materials, and also of material No. II from Le Tiel, were ground to pass the 0·09-mm. sieve. The material from Buenos Aires was already finely divided. Small quantities of each of these four materials were made into paste with distilled water and burnt for 45 minutes at 1450 deg. C. after gradually approaching that temperature. The free lime and chemical compositions of the resulting clinkers were determined. The silicate moduli and free-lime contents were as follows: Bologna, 5·5, 0·14; Novorossiysk, 12·8, 0·55; Le Tiel (No. II), 21·3, 6·08; Buenos Aires, 5·5, 2·89. All four clinkers were hard.

The next part of the investigation concerned only the samples from Bologna and Novorossiysk. A quantity of 4 kg. to 5 kg. of each of these raw materials was ground in a ball mill until 85 per cent. passed the 0·09-mm. sieve. The powder was made into sausage-shaped forms with water and burned for 40 minutes at 1450 deg. C. in an oil-fired chamber kiln. Up to 1100 deg. C. the temperature was raised at the rate of 10 deg. per minute, and then at 1·5 deg. per minute up to the burning temperature. After firing, the clinker was raked out as quickly as possible and cooled in air. These clinkers were ground to cement with 3 per cent. of gypsum. Compressive strengths varied between 2200 lb. and 4700 lb. per square inch at three days, and between 2900 lb. and 6300 lb. per square inch at seven days, according to the operation of the kiln and the fineness of grinding. The only apparent cause of this favourable behaviour appeared to be the extreme fineness of the particles of quartz; no other indication was obtained by chemical, X-ray, or microscopical examinations.

Using quartz with a specific surface of 16,000 sq. cm. per gramme and pure calcium carbonate, ferric oxide, and alumina, clinkers were made on a small scale by the same burning process as before, using an ascending silicate modulus and determining the amount of free lime in each clinker. With a silicate modulus up to 20, the free lime was less than 1 per cent.; at a modulus of 35, the free lime was 4 per cent.; above 45 the free lime remained at 5 per cent.

Using precipitated silica (containing 12·6 per cent. of water and with a specific surface of 32,000 sq. cm. per gramme) and the same pure components, the free

lime increased much more rapidly with rise in silicate modulus; at modulus 12 the content of free lime was already 4 per cent., and only the use of materials with lower moduli resulted in hard clinker.

Trials were made with several kilogrammes of material based on quartz flour and having a silicate modulus of 30 to 70. The burning period was 2½ hours. In spite of the negligible amounts of aluminate and ferrite, strengths increased with additional amounts of gypsum. Cements gave normal results in the Le Chatelier test, and compressive strengths up to 2800 lb. per square inch at three days, 4250 lb. at seven days, 5400 lb. at 14 days, and 6900 at 28 days. It is pointed out that tricalcium silicate produces only half the strength of best Portland cement at 28 days, but has the same strength at one year.

Ten mixtures were burnt in small-scale tests changing only the specific surface of the quartz flour (97 per cent. SiO_2). The mixtures, consisting of 17·8 per cent. quartz flour and 82·2 per cent. calcium carbonate, were burned for 45 minutes. At first the content of free lime in the clinker was reduced linearly with increase in specific surface of the quartz, but at a specific surface of 14,000 sq. cm. per gramme it suddenly became constant, and at 21,000 sq. cm. per gramme there was little difference. Ground quartzite gave a similar result, with the sudden change at a specific surface of 13,000 sq. cm. per gramme. Higher temperatures and increased time of burning resulted in small decreases in content of free lime, but the change occurred at the same specific surface.

Ground quartz was converted into cristobalite by protracted heating at 1500 deg. C. At a specific surface of 15,000 sq. cm. per gramme and above, the cristobalite showed slightly less combination than quartz, but at the normal fineness of 4,000 to 6,000 sq. cm. per gramme the cristobalite reacted considerably less than the quartz. Trials with non-crystalline quartz glass showed a linear increase in combination with increase in specific surface from 10,000 to 22,000 sq. cm. per gramme, but even at the highest value the content of free lime was greater than in all the cases in this range using crystalline quartz.

Testing Cements with Fine Sands.

In "Archiwum Inzynierii Ladowej," Vol. IV (1958), No. 4 (published in Warsaw), Mr. Tadeusz Szulczynski describes some tests on cement mortars made with sand ground to the same degree of fineness as the cement. The proportion of water absorbed by this sand is practically equal to the amount absorbed by the cement, thereby removing one of the causes of the different results obtained from tests in which standard sands of different gradings are used. With such finely-ground sand a standard consistency of the mortar may be obtained by specifying the ratio of the quantity of water to that of the dry mixture of cement and sand. The water-cement ratio may then be varied by altering the ratio of cement to sand without changing the specified amount of water.

Tests made in France by M. L. Chassevent are also described; these confirm that the natural degree of fineness of the sand and its origin have little effect on the results of standard tests of cement mortars containing finely-ground sands.

Heat-resistant Cement.

THE Technical News Bulletin for January, 1959, of the U.S. National Bureau of Standards includes a report of an investigation on the mechanism of high-alumina cement at high temperatures as in the case of refractory concrete made with high-alumina cement and heat-resisting aggregates. Such concrete is used for lining furnaces, and it is also used in the missile-launching pads at Cape Canaveral, Florida, U.S.A. An attempt was made to relate any changes in composition following heat treatment to changes in physical properties. In general, the results showed a significant correlation between changes in mechanical properties and compound composition.

Four commercial high-alumina cements, two American and two others, having a fairly wide range of silica and iron-oxide content were investigated. A water-cement ratio of 0·25 was used to prepare test specimens of two sizes, namely 1 in. by 1 in. by 7 in. and 1 in. by 1 in. by 12 in. The hydrated specimens were cured for 28 days at 25 deg. to 27 deg. C. and between 95 and 100 per cent. relative humidity prior to heat treatment. All heat treatments at 200 deg. C. and above were in a furnace heated by silicon-carbide resistance elements at the rate of about 100 deg. C. per hour with a soaking period of two hours at the higher temperatures. For heat treatments below 200 deg. C. the specimens were placed directly in a drying oven, which was then maintained at the desired temperature for 48 hours.

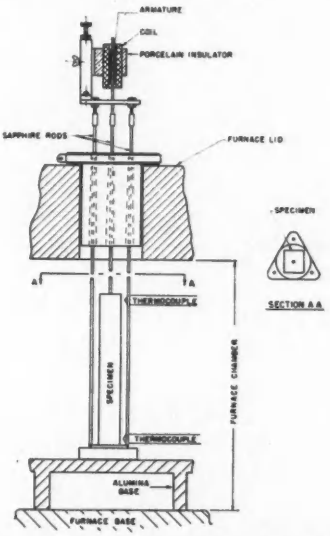
Both X-ray diffraction and differential thermal analysis were used for compound identification. X-ray patterns were made at room temperature before and after hydration of each cement and after heat treatment of the hydrated specimens. Differential thermal analyses were made by placing a cement sample and a reference material in a furnace and increasing the temperature at the rate of 8·5 deg. C. per minute. The temperature of the cement sample and its deviation from that of the reference material were continuously recorded during the heating period.

The dehydration characteristics of three hydrates commonly found in hydrated high-alumina cements were also studied to facilitate the identification of the hydrated constituents of the cement specimens. These compounds were $CaO{\cdot}Al_2O_3{\cdot}10H_2O$, $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$, and $Al_2O_3{\cdot}3H_2O$. Differential thermal analysis patterns showed characteristic endothermic peaks for the three compounds as well as for the hydrated specimens prepared from the commercial cements. The number of peaks indicated that dehydration of the samples occurred in a stepwise process common to many types of clays.

Young's modulus of elasticity was determined for the 1-in. by 1-in. by 12-in. specimens before and after heat treatment. A sonic method was used in which the specimen was vibrated in flexure. This vibration is sensed by a phonograph pick-up and passed to an oscilloscope, where the resonant frequency is located by means of Lissajous figures. The resonant frequency is determined from an electronic frequency counter and is used to calculate Young's modulus.

Upon completion of the dynamic elasticity measurements, the specimens were placed in a transverse testing apparatus and loaded to failure. Changes in length with changes of temperature were measured with a dilatometer for hydrated specimens that had received no prior heat treatment. The specimens were placed in a furnace and data obtained for two separate heating and cooling cycles.

It was found that elasticity and strength decreased between room temperature and 50 deg. to 75 deg. C. because of the partial dehydration of $CaO \cdot Al_2O_3 \cdot 10H_2O$ and the formation of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $Al_2O_3 \cdot 3H_2O$. However, the specimens showed a high rate of expansion up to about 110 deg. C. Between 75 deg. C. and 110 deg. C. the strength increased because of increased crystallinity of $3CaO \cdot$



Apparatus Used to Measure Changes in Length.

$Al_2O_3 \cdot 6H_2O$ and $Al_2O_3 \cdot 3H_2O$. At about 100 deg. C. to 300 deg. C. to 500 deg. C. the strength and the expansion rate decreased because of complete dehydration of all three hydrates. The modulus of elasticity was relatively constant in the range from 300 deg. to 500 deg. C. to 1100 deg. C., indicating that elasticity is less sensitive to changes in composition and structure. Above 700 deg. C. all cements exhibited decreased strengths. Above 800 deg. C. differences became apparent in the length changes of the four cements because of differences in composition. Also, sintering occurred at these high temperatures, resulting in rapid contraction of the cement.

Thus, the laboratory studies showed that many changes in the mechanical properties of high-alumina cements are directly related to corresponding changes

in compound composition. For example, the dehydration of $CaO{\cdot}Al_2O_3{\cdot}10H_2O$, $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$, and $Al_2O_3{\cdot}3H_2O$ produced an over-all reduction in strength and modulus of elasticity as well as an appreciable contraction of the cements. Also, the grain size, crystallinity, and sintering characteristics of each constituent compound and the solid state reactions between these compounds influenced the mechanical properties to varying degrees.

Production of Cement Abroad.

China.

It is reported that 5,000,000 tons of cement were produced in China in the first six months of 1959.

Jordan.

Production of the cement works at Salt, Jordan, was 106,000 tons in the year 1958. The consumption of cement in Jordan last year was 160,000 tons.

Poland.

The cement works now being built at Nowa Huta has started production. The capacity of the works is to be 1,000,000 tons a year, and it is expected to be completed in 1962.

Sudan.

It is estimated that 95,000 tons of cement were produced in Sudan during 1958.

Mexico.

The production of cement in Mexico in the year 1958 was 2,500,000 tons.

Formosa.

The production of cement in Formosa is now at the rate of 1,000,000 tons a year, of which 300,000 tons are available for export.

Madagascar.

The production of cement at the factory at Amboanio, near Majunga, was at the rate of 250 tons a month at the end of the year 1958, and it is estimated that 50,000 tons will be produced this year.

Nicaragua.

The production of cement in Nicaragua in the year 1958 amounted to 39,350 tons; in the previous year 42,000 tons were made.

Dominican Republic.

The capacity of a cement factory at Ciudad Trujillo is being increased. The quantity of cement exported in the first six months of 1958 was 23,886 tons compared with 30,246 tons in the first six months of 1957.

The Use of Calcium Chloride in Filtering Slurry.

EXPERIMENTS have been made by the Columbia-Southern Chemical Corporation of the U.S.A. in the use of calcium chloride in cement manufacture, particularly in the slurry filtration process. The following is an abstract of some notes on this subject contributed to " Pit & Quarry " (December 1958) by Mr. E. Carl Kreager and Mr. Eugene W. Geary.

At one of the Corporation's cement works the rate of production of the filter wheels was suddenly reduced to about one half of normal. The cake from the wheels was high in moisture content and very gummy. There were no mechanical defects in the wheels. The use of open-pit limestone quarries had been abandoned in favour of mining. The percentage of clay in the mixture was not in excess of that in the mixture previously used.

The capacity of the filter wheels had always been inadequate unless the material was flocculated by adding hydrated lime, but this method had failed completely. Since the limestone and shale, or clay, used were the same, it was decided that the trouble was caused by adventitious salts present in the limestone from the mine but which were not present in the quarried stone. Various flocculating agents were tried in the laboratory without success until calcium chloride was tried, and when the calcium chloride treatment was used in the plant the filtration rate immediately returned to normal. Some of the adventitious salts found in the mine were soluble iron and aluminium, sulphates, and sulphides.

It is assumed that in the filtration of fine particles, especially of flat clay particles, dispersion is not conducive to high filtration rates During the filtration of dispersed slurry the particles form a blanket of closely piled layers, which makes it difficult to extract the water from the upper layers. Flocculation of the slurry, on the other hand, results in random piling, with extensive voids, through which water can escape in the filtration or the thickening operations. Dispersion is promoted by dilution, by hydrous surfaces of the particles, by similar electrical charges on the surfaces of the particles, or by protective colloids. Flocculation, on the other hand, is promoted by the addition of a suitable amount of electrolyte to discharge the particles, by thick pulps, and sometimes by heating, unless this promotes the solution of the dispersing salts. The addition of salts which precipitate as insoluble compounds the salts that have a dispersing action is also effective. Heating probably promotes flocculation by reducing the surface tension and viscosity of the water.

Since lime is a satisfactory electrolyte in many cases, and since it promotes flocculation, it is probable that when certain salts are present lime promotes precipitation of particles with hydrous surfaces, with consequent dispersion and poor filtration rates. Calcium chloride, on the other hand, acts as a true electrolyte; it tends to discharge the particles, and results in flocculation and random piling, with good rates of filtering.

A standard water-hardness test on the filtrate was correlated with the production rates of the filters and additions of calcium chloride. It was found that

filtering rates increased rapidly until a rate of 800 parts per 1,000,000 was reached, but beyond this rate the gain was less. This standard has been used for several years. It is recognised that this type of control would not result in the same addition of calcium chloride to other raw materials. The requirements vary widely, depending on the type and quantity of dispersing salts present.

New Cement Works Abroad.

The Philippines.

The erection of a cement works by the Clep Cement Corporation in Padre Burgos Quezon, has been approved by the National Economic Council. The capacity is to be 1,250,000 tons a year, and the cost of the works is estimated to be about £1,800,000.

Ceylon.

The Government of Ceylon is considering the erection of a new cement works and the extension of the existing cement works at Kankesan.

Colombia.

A new cement works at Manizalez started production on June 1 last.

El Salvador.

Among otner industrial projects being planned in El Salvador are factories for the production of cement.

Thailand.

The Siam Cement Co. is to extend its works by the addition of a rotary kiln and a cement mill, at a cost of about £270,000. The equipment will be bought from F. L. Smidth & Co., of Denmark.

Peru.

The new cement works for Cemento Andino S.A., at Tarma, Peru, commenced operation in December 1958 and has initially a daily output of 700 bags (about 30 tons) of cement.

Hungary.

The cement and lime works at Tatabánya, Hungary, is to be reconstructed at a cost of about £4,000,000; the new plant is designed to enable poor quality brown coal to be used. The cement and lime works at Lábatlan is also being modernised and extended at a cost of about £10,000,000; the new works will have a capacity of 520,000 tons a year.

India.

The production of cement in India was 6,060,000 tons in 1958 compared with 5,600,000 tons in 1957. Two new cement works commenced operation in 1958. There are now 31 works.

The Iron-bearing Phase in Portland Cement Clinker.

AN investigation of the pseudo ternary system calcium oxide-monocalcium aluminate ($CaO.Al_2O_3$)-dicalcium ferrite ($2CaO.Fe_2O_3$), by Mr. T. F. Newkirk and Mr. R. D. Thwaite, is reported in the Journal of Research of the U.S. National Bureau of Standards for October 1958.

Following an account of their work, the authors state that the extent to which information on the ternary system can be applied directly to the manufacture of Portland cement clinker containing many components is limited. Nevertheless, because of the similarity of the phases actually observed in commercial clinkers to some of those appearing in simpler systems, useful extrapolations of phase relations in these systems can help to explain the behaviour of the more complex compositions.

It is generally conceded, as a result of previous investigations, that the principal iron-bearing phase in Portland cement clinker is essentially a calcium alumino-ferrite of variable composition. In commercial clinkers it is likely that this phase contains also small amounts of additional components in solid solution. It is evident that even the composition of the final Fss phase, formed by complete equilibrium crystallisation, can vary widely with different mixtures in the system. This variability results from the fact that there are wide ranges of composition (the six 2-phase areas) for which crystallisation is completed on a phase boundary rather than at an invariant point. The variability applies to the temperature at which liquid is first formed or disappears in the different mixtures as well as to the composition of the Fss phase. Only in the single-phase Fss region and the two-phase CaO-Fss region will the Al_2O_3/Fe_2O_3 ratio of the Fss phase always be the same as that of the original mixture.

The one-phase and two-phase areas in the ternary system may be expected to bound analogous regions in multicomponent clinker systems in which both the final composition of the Fss phase and the solidus temperature will vary with the composition of the mixture. Even if equilibrium were attained, therefore, for commercial Portland cement clinkers the temperature at which liquid is first formed during burning, the quantity of liquid produced in the hot zone of the kiln, and the constitution of the clinker can differ considerably in cement raw mixtures of different Al_2O_3/Fe_2O_3 ratios. The Al_2O_3/Fe_2O_3 weight ratio in the iron-bearing phase can presumably vary with different mixtures from 0 to 1·476, with accompanying effects on the percentages of the other constituents of the clinker.

Although the presence of Fe_2O_3 in the mixture causes the formation of a liquid phase at a lower temperature than if it were absent, increasing the percentage of Fe_2O_3 in the raw mixture does not necessarily cause easier burning, but may have the opposite effect. Mixtures whose crystallisation is completed along the CaO-Fss phase boundary, or at E_1 (eutectic temperature, 1,389 deg. C.) will be more difficult to burn than mixtures completing their crystallisation at invariant points E_2 and E_3.

Optimum conditions for proportioning and burning raw materials of known chemical compositions to produce clinker of the desired constitution and burning

characteristics cannot be determined from the phase diagram for the ternary system alone. Additional work is still required on portions of the quaternary system CaO-Al_2O_3-Fe_2O_3-SiO_2. Specifically needed in the four-component system are additional tie lines showing the compositions of the Fss phase in equilibrium with liquids along phase boundaries, and a further subdivision of the system into composition spaces that define the final products of crystallisation within each region.

Prevention of Accidents.

The report for the year 1958 of the Accident Prevention Advisory Committee of the Cement Makers' Federation shows a remarkable reduction in the number of accidents since the committee was formed in the year 1950. In 1950 there were 550 accidents reported. In 1958 there were 254. The most common form of accident is falling from a height, and a special effort to draw attention to this cause of injury resulted in the number of such accidents falling from an average of 89 in the four years 1954 to 1957 to 52 in 1958. The number of man-hours lost at cement works due to accidents was 54,614 in 1959, compared with 71,344 in the previous year; the time lost from work due to each accident, was, on average, about one month.

There were three fatal accidents last year. In one case a man was found dead at the end of a conveyor; it was presumed that he had followed a shovel into the nip between the belt and the idling pulley in an attempt to clear an obstruction. In another case a steeplejack fell through a gap while putting new sheets on a kiln house. In the last case a man was crushed between a railway wagon and a tractor while shunting the wagon; it appears that he had improvised a means of doing so with the aid of a rope-sling which became entangled in the wheels of the tractor and pulled the tractor towards the wagon where he was standing.

Limestone Deposits in South Vietnam.

A geological survey is to be carried out in the Ha Tien district of South Vietnam where limestone deposits exist from which it is estimated that some 150,000 tons of cement a year could be produced.

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Transport of Loose Cement.

THE illustrations show a method introduced by the North-Eastern Region of British Railways for the transport of loose cement. The railway wagon (*Fig.* 1), known as the " Presflo," has a capacity of 20 tons and more than 900 of them are now in use for the transport of Portland cement. These wagons operate in conjunction with pressurised road vehicles, two of which are now in operation at the Marsh Lane goods depot at Leeds. The cement is transferred from the rail wagon to the road vehicle by compressed air through a flexible pipe of 4 in. diameter at the rate of 1 ton a minute. The blower provides 300 cu. ft. of free air per minute at a maximum pressure of 12 lb. per square inch. The road vehicle has a capacity

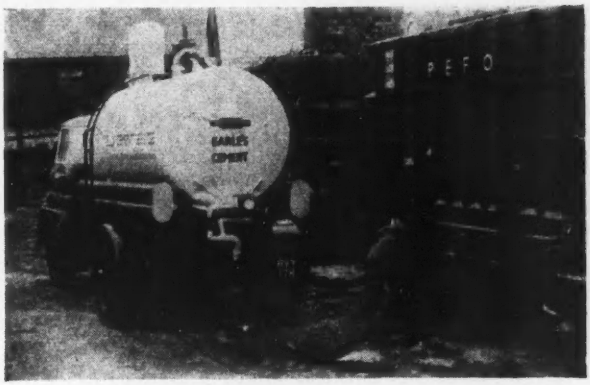


Fig. 1.—Transferring Cement from Railway Wagon to Road Vehicle.

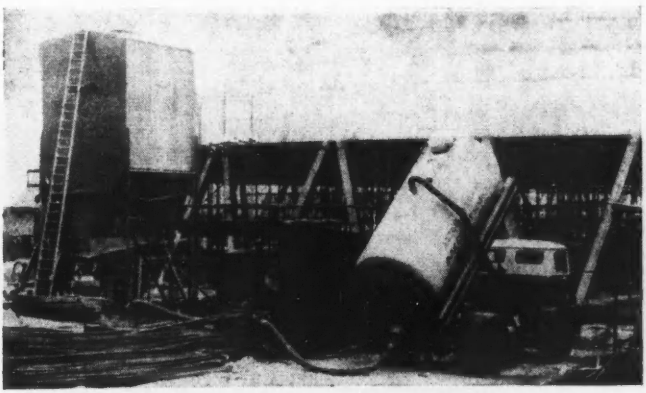


Fig. 2.—Transferring Cement from Road Vehicle to Silo.

of 210 cu. ft. The cement is discharged from the road vehicle to the silo through a jet at the rear of the tank, and its flow may be assisted by tipping the tank (*Fig.* 2). The cement can generally be transferred from the vehicle to the silo at the rate of 1 ton a minute.

Patent Applications.

Composition of Cements.

A high-grade Portland cement clinker of low magnesium and iron content is obtained as a by-product when a mixture of beta-spodument, sand, limestone, and calcium chloride is roasted during the preparation of lithium carbonate.—No. 804,962. Chemical Patents, Inc. October 9, 1956.

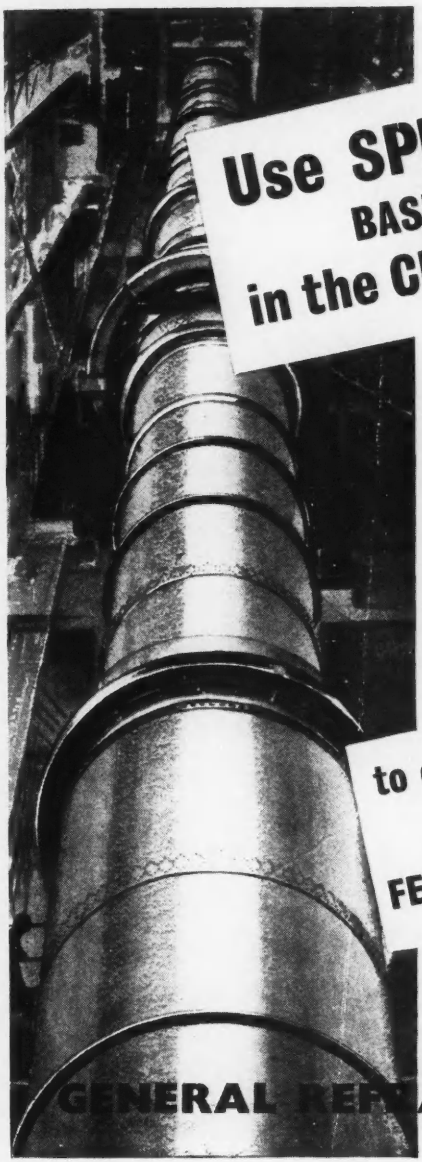
A cementitious composition comprises hydraulic cement as a major constituent, and, as minor constituents, water and a water-insoluble film-forming polymer or co-polymer derived from at least one water-insoluble monomer of the formula $RC = CH_2—COOR^1$ wherein R is one of the group H ; alkyl l_nH_{2n} 1 ; phenyl, tolyl ; xylyl ; or benzl : R^1 is of the same group but excluding H : the polymer being convertible intrinsically from particulate to continuous film form at not higher than room temperature. Specified cements are Portland, white, aluminous, natural, pozzolanic, and slag. Preferred polymers are polyacrylic latices. Optional ingredients are sand, clay, pigments, glass, emery, slag, gravel, sodium silicate, carboxy methyl-, methyl-, ethyl-cellulose, iron filings, asbestos, or glass fibres.—No. 804,358. Master Mechanics Co., June 8, 1956.

Moisture-resistant Cements.

A minor proportion of a mixture of oleic acid and a phenol is added to cement during or subsequent to the grinding stage of manufacture to render it moisture resistant during storage. The preferred amount is 0·25 to 2·0 per cent. and the preferred proportions are oleic acid 20 to 30 per cent. : 70-80 phenol, for example chlorinated cresylic acid. Homogeneous distribution of the mixture throughout the cement is attained by grinding the clinker and mixture together.—No. 797,819. C. L. Walsh, March 4, 1957.

Cement is made water repellent during storage by the addition during or after the grinding stage of its manufacture of a minor proportion of low temperature carbonaceous oil product derived from a waxy distillate of Middle Eastern crude oil, of boiling point 150 deg. to 400 deg. C. The preferred amount is 0·01 to 2 per cent.—No. 801,652. C. L. Walsh, June 2, 1955.

Cement is made water repellent by adding 0·5 to 1 per cent. of a long-chain organic compound, having at least 8 carbon atoms and a water-repelling group at one end and a water-attracting group at the other end of the chain, to cement clinker and grinding in a mill. Specified compounds are tail oil and a gum extract from the refining of petroleum lubricating oils. Soil can be stabilised with the modified cement.—No. 762,669. D. S. Grant and L. W. Lyon, October 5, 1954.



Use SPINELLA A/C BASIC BRICKS in the Clinkering Zone

Refractory service conditions are generally most severe in the "clinkering zone", where the final clinkering or incipient fusion of the charge takes place, it is in this zone that refractory replacements are most extensive. Generally, the satisfactory performance of any refractory used in this zone is dependent upon the formation and retention of a clinker coating, which minimises chemical attack and thermal shock. When conditions of chemical corrosion are particularly severe, Spinella "A/C", a basic brick, is necessary.

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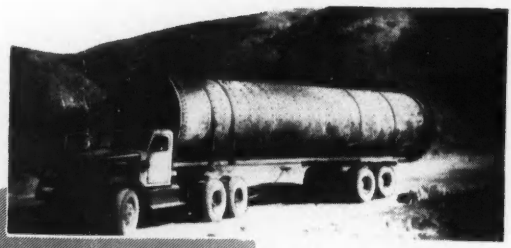

An 8ft. 6in. diameter Tube Mill on route to the new plant.

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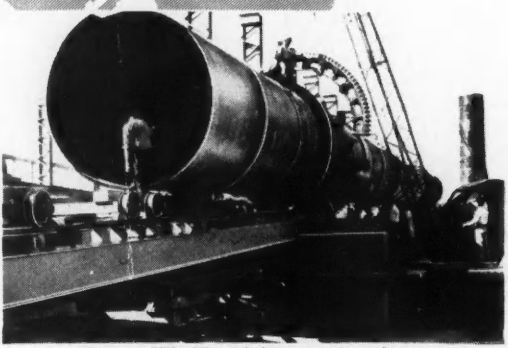

Rotary Kiln No. 1 being erected on site.

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